PHYSICS AND CHEMISTRY OF SOLID STATE
V. 26, No.2 (2025) pp. 285-295
Section: Chemistry

DOI: 10.15330/pcss.26.2.285-295

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 26, № 2 (2025) С. 285-295
Хімічні науки

UDC: 546.786'64'32'33'39'46'47:546.05:543.442.3:543.427.34

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

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Phase Formation in the Systems A^+–Y^{3+}– WO_4^{2-}–H^+–H_2O ($A^+ = NH^{4+}$, K^+) and M^{2+}–Y^{3+}– WO_4^{2-}–H^+–H_2O ($M^{2+} = Mg^{2+}$, Zn^{2+}). Synthesis, FT-IR Spectroscopy, and Crystal Structure Determination of Salts with Paratungstate B Anion, $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot12H_2O$ and $K_{10}[W_{12}O_{40}(OH)_2]\cdot13H_2O$

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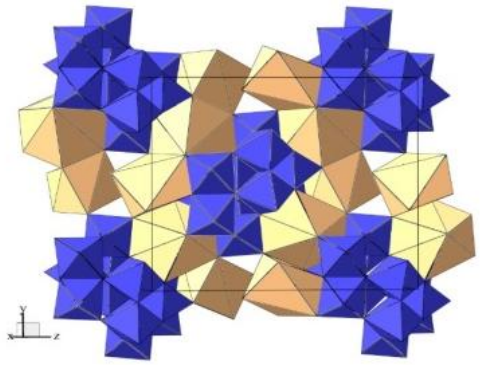

A new procedure for the synthesis of sodium heteropoly decatungstoyttriate(III) $Na_9[Y(W_5O_{18})_2]\cdot35H_2O$ (I) from an aqueous solution of sodium tungstate, acidified to $Z = \nu(H^+)/\nu(WO_4^{2-}) = 0.80$ with a ratio of $\nu(Y):\nu(W) = 1:10$ and with 2-propanone adding, has been developed. The presence of the Peacock–Weakley type anion in the obtained salt has been confirmed by FTIR spectroscopy. The micromorphology of the surface was studied using scanning electron microscopy (SEM); it was found that the grain size of (I) is in the range of 200–450 nm. The single-phase nature of the synthesized salt was confirmed by the uniform contrast of the surface in the backscattered electron mode.

The conditions for the synthesis of salts with the paratungstate B anion $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot12H_2O$ (II), $K_{10}[W_{12}O_{40}(OH)_2]\cdot13H_2O$ (III), and $M_5[W_{12}O_{40}(OH)_2]\cdot nH_2O$ ($M^{2+} = Mg^{2+}$ (IV), and Zn^{2+} (V)) from acidified with $Z = 0.80$ aqueous solutions of the systems A^+–Y^{3+}–WO_4^{2-}–H^+–H_2O ($A = NH_4^+$, K^+) and M^{2+}–Y^{3+}–WO_4^{2-}–H^+–H_2O ($M^{2+} = Mg^{2+}$, Zn^{2+}) have been established. Elemental analysis, SEM, and FTIR spectroscopy characterized the obtained salts.

The crystal structure of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot12H_2O$ (II) ($M_r = 3286.72$, orthorhombic, Pbca, $a = 14.0631(6)$ Å, $b = 15.6713(5)$ Å, $c = 22.9147(16)$ Å, $V = 5050.1(4)$ Å^3 at $T = 200(2)$ K, $Z = 4$, $d_{calcd} = 4.323$ g/cm^3) and $K_{10}[W_{12}O_{40}(OH)_2]\cdot13H_2O$ (III) ($M_r = 3489.42$, monoclinic, $P2_1/c$, $a = 11.5049(6)$ Å, $b = 14.3008(7)$ Å, $c = 15.4567(10)$ Å, $\beta = 105.889(7)°$, $V = 2445.9(2)$ Å^3 at $T = 293(2)$ K, $Z = 2$, $d_{calcd} = 4.738$ g/cm^3) was determined by single crystal X-ray analysis.

Keywords: polyoxometalates, heteropoly tungstate, yttrium, Peacock–Weakley type of structure, paratungstate B anion, scanning electron microscopy, single-crystal X-ray diffraction, synthesis.

Received 07 October 2024; Accepted 09 April 2025.

Introduction

The number of papers dedicated to yttrium(III)-containing polyoxometalates (POMs) is significantly lower than those describing lanthanoid(III)-containing POMs. Formally, yttrium is not a lanthanoid, but it can be considered as a pseudo-lanthanoid due to its close ionic radius and characteristic coordination numbers.

The first yttrium (III)-containing POM was described in 1971 by R. D. Peacock and T. J. R. Weakley [1]. The crystal structure of the compound with the anion $[YW_{10}O_{36}]^{9-}$ and its properties in solution were studied using ^{183}W and ^{89}Y NMR [2]. This polyanion consists of two monolacunary tetradentate fragments $[W_5O_{18}]^{6-}$, derived from the hexatungstate anion with Lindqvist structure, which encapsulates the central Y^{3+} ion, forming a polyhedron $\{YO_8\}$ in the shape of a square antiprism. Another class of yttrium and lanthanoid derivatives of POMs is isopoly tungstates, which are isopoly anions composed of 22 octahedra WO_6 $\{W_{22}\}$, to which two Y(III)/Ln(III) ions are coordinated – $[M_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{8-}$ (M^{3+} = Y, La, Ce, Tb, Dy, Ho, Er, Tm, Yb, Lu) [3]. The Y(III)-containing acetate-bridged dimeric undecatungstate $[Y(CH_3COO)XW_{11}O_{39}(H_2O)]^{6-}$ (X = Si^{4+} and Ge^{4+}) is described in [4]. Kortz et al. [5] reported the synthesis of a new series of heteropoly oxopalladates encapsulating yttrium(III) and lanthanoids(III), $[X^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$ (X = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb i Lu), in which the cuboidal polyanions consist of a capsule with twelve Pd^{2+} ions linked to eight terminal phenylarsenate heterogroups, with guest ions located in the center of the cavities. Also, in [6], a Y(III)-containing tungstophosphate $[(PY_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$ is described, and in [7], a salt with the heteropoly anion $[\{Y_4(\mu_3\text{-}OH)_4(H_2O)_8\}(R\text{-}P_2W_{15}O_{56})_2]^{16-}$ with a Wells–Dawson structure is studied. Furthermore, in [8], a Y(III)-containing 40-tungsto-4-arsenate(III) $[Y(H_2O)_5\{Ni(H_2O)\}_2As_4W_{40}O_{140}]^{21-}$ was studied, and in [9], a trimeric tungstoantimonate(III) $[\{Y(R\text{-}SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)]^{17-}$ is characterized. However, the salt $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ remains the only Y(III)-containing heteropoly tungstate with an anion of the Peacock–Weakley type of structure [1, 2], and there is currently no information regarding the possibility of obtaining salts with other cations besides Na^+ in contemporary works.

In this study, we present the results of the development of a new procedure for the synthesis of the heteropoly salt $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I) with the Peacock–Weakley type of anion, which is implemented through self-assembly from WO_4^{2-} and Y^{3+} in an acidified aqueous solution with a stoichiometric ratio of reagents, followed by precipitation using 2-propanone. We also report the use of the $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ solution as a precursor for obtaining individual salts with the paratungstate B anion using single-charged (NH_4^+, K^+) and double-charged (Mg^{2+} and Zn^{2+}) cations. The study establishes that only salts with the paratungstate B anion – $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (II), $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (III), $Mg_5[W_{12}O_{40}(OH)_2]\cdot 41H_2O$ (IV), and $Zn_5[W_{12}O_{40}(OH)_2]\cdot 35H_2O$ (V) can crystallize from the systems $A^+–Y^{3+}–WO_4^{2-}–H^+–H_2O$ (A^+ = NH_4^+, K^+) and $M^{2+}–Y^{3+}–WO_4^{2-}–H^+–H_2O$ (M^{2+} = Mg^{2+}, Zn^{2+}).

I. Experimental

Reactants. Aqueous solutions of $Na_2WO_4\cdot 2H_2O$, $Y(NO_3)_3\cdot 6H_2O$, and HNO_3 (all are ACS reagent grade) were used in this work. The exact concentrations of Na_2WO_4 (C = 0.5663 mol/L), HNO_3 (C = 0.3467 mol/L), and $Y(NO_3)_3$ (C = 0.1054 mol/L) were determined using procedures previously described in [10-11]. For the isolation of sodium heteropoly decatungstoyttriate(III), 2-propanone $(CH_3)_2CO$ (analytically reagent grade) was used. Solutions of NH_4NO_3 (C = 2.0 mol/L) and KNO_3 (C = 2.0 mol/L) were prepared by dissolving NH_4NO_3 and KNO_3 (all are analytically reagent grade) in distilled water. A solution of $Mg(NO_3)_2$ (C = 0.5224 mol/L) and a solution of $ZnSO_4$ (C = 0.7244 mol/L) were prepared by dissolving $Mg(NO_3)_2\cdot 6H_2O$ and $ZnSO_4\cdot 7H_2O$ (both are analytically reagent grade) in distilled water. The concentrations of Mg(II) and Zn(II) were determined by direct complexometric titration with the solution of Trilon B (reagent grade) in an ammonia buffer solution with pH 9.2 (with eriochrome black T indicator) (δ = 0.8%).

Synthesis Methodology. The synthesis of $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I) was carried out as follows. A solution of sodium tungstate (17.66 mL, C = 0.5663 mol/L) was added to 49.78 mL of distilled water, and slowly, while stirring vigorously, a solution of HNO_3 (23.07 mL, C = 0.3467 mol/L) was added. Then, dropwise and with vigorous stirring, a solution of $Y(NO_3)_3$ (9.49 mL, C = 0.1054 mol/L) was added. Each subsequent drop of $Y(NO_3)_3$ was added only after the opalescence from the previous drop had disappeared. The final volume of the aqueous solution was 100 mL. The addition of reactants in the specified amounts corresponds to the reaction stoichiometry forming the anion of heteropoly decatungstoyttriate(III), $[Y(W_5O_{18})_2]^{9-}$. Then, 100 mL of 2-propanone was added to the solution to isolate the salt as a solid phase. The resulting product was hermetically sealed and stored for 3 days at 279 K which led to the formation of a colorless needle-like crystalline precipitate.

The synthesis of compounds with NH_4^+, K^+, Mg^{2+}, and Zn^{2+} cations was carried out using the following methodologies. The solutions of NH_4NO_3 (C = 2 mol/L, V = 5; 10 mL), KNO_3 (C = 2 mol/L, V = 5; 10 mL), $Mg(NO_3)_2$ (C = 0.5224 mol/L, V = 8.61 mL), and $ZnSO_4$ (C = 0.7244 mol/L, V = 6.21 mL) were added to the solutions of (I) (C = 0.010 mol/L, V = 100 mL) with vigorous stirring.

It should be noted that immediately after the addition of $ZnSO_4$, a white precipitate was formed. In contrast, adding other cations did not lead to immediate precipitation. After holding the solutions under laboratory conditions in the air for 15 days, the formation of colorless crystals was observed. These crystals were separated by filtration (using a "blue ribbon" paper filter), washed with distilled water, dried in air to a constant mass, and used for analysis.

Chemical analysis of salts. The content of

tungsten(VI) was determined gravimetrically as WO_3 ($\delta = 0.5\%$), while the contents of Y^{3+}, Mg^{2+}, and Zn^{2+} were determined by direct complexometric titration ($\delta = 0.5\%$). The sodium or potassium content ($\delta = 1\%$) was determined using atomic absorption spectroscopy (Saturn–3 Spectrometer; air/acetylene flame, $\lambda = 589.0$ nm for Na^+, $\lambda = 766.5$ nm for K^+, high-frequency electrodeless lamp VSB-2, I = 70 mA). The content of H_2O in the salts was determined by isothermal calcination of precise weights at 823 K ($\delta = 0.5\%$).

Results of chemical analysis of colorless crystals of $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I): calculated (wt.%) – Na_2O 8.4; Y_2O_3 3.4; WO_3 69.4; H_2O 18.9; found (wt.%) – Na_2O 8.2; Y_2O_3 3.2; WO_3 69.1; H_2O 18.9. Yield 90%.

Results of chemical analysis of colorless crystals of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (II): calculated (wt.%) – Na_2O 1.9; WO_3 84.6; found (wt.%) – Na_2O 1.8; WO_3 84.3. Yield 70%.

Results of chemical analysis of colorless crystals of $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (III): calculated (wt.%) – K_2O 13.4; WO_3 79.4; H_2O 7.2; Found (wt.%) – K_2O 13.3; WO_3 79.1; H_2O 7.2. Yield 77%.

Results of chemical analysis of colorless crystals of $Mg_5[W_{12}O_{40}(OH)_2]\cdot 41H_2O$ (IV): calculated (wt.%) – MgO 5.4; WO_3 74.4; H_2O 20.2; found (wt.%) – MgO 5.6; WO_3 74.5; H_2O 20.3. Yield 44%.

Results of chemical analysis of colorless crystals of $Zn_5[W_{12}O_{40}(OH)_2]\cdot 35H_2O$ (V): calculated (wt.%) – ZnO 10.6; WO_3 72.5; H_2O 16.8; found (wt.%) – ZnO 10.4; WO_3 72.1; H_2O 16.8. Yield 60%.

FTIR Spectroscopy. FTIR spectra were recorded for air-dried samples compressed into a crystalline KBr matrix (the sample content in the KBr matrix was 0.5 wt.%) using the FTIR Spectrum BXII spectrometer (Perkin–Elmer) in the wavenumber range of 400-4000 cm^{-1}.

Microscopic analysis. Microscopic studies were carried out using scanning electron microscopy (SEM) using a JSM-6490LV (JEOL) microscope. Air-dried samples were mounted on graphite tape and examined in the backscattered electron (BEC) mode, which was used to establish the phase homogeneity of the synthesized samples. The surface micromorphology of the obtained salts was studied in the secondary electron imaging (SEI) mode. Elemental analysis during microscopic studies was carried out using an INCA Wave-500 Wavelength Dispersive X-ray spectrometer. Energy dispersive X-ray analysis was carried out on the surfaces of powders with different areas and at specific points on the surface. The results of the elemental analysis were consistent with the results of classical chemical analysis, e.g., for (I), the found molar ratio of elements Y:Na:W = 1.00:8.99:9.83 coincided with the theoretical one (Y:Na:W = 1.00:9.00:10.00).

Single crystal X-ray diffraction analysis. The single crystal X-ray diffraction analysis of the single crystals of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (II) and $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (III) was carried out using a Single-Crystal X-ray Diffractometer Xcalibur-3 (Oxford Diffraction) with MoK_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and a Sapphire-3 CCD detector. For salt II, ω/θ scanning was performed in the range of $6.30 \le 2\theta \le 60°$, resulting in 30,781 measured reflections. For salt III, ω/θ scanning was performed in the range of $6.18 \le 2\theta \le 59.98°$, resulting in 16,175 measured reflections. The solution and refinement of the structures were carried out using the SHELX-97 software [12]. Structural analysis and figure creation were performed using WinGX [13] and Ball&Stick [14]. The presence of heavy atoms hindered the localization of hydrogen atoms in both structures.

II. Results and discussion

Most known POMs have been obtained through self-assembly from mononuclear starting components (MO_4^{n-}, and X^{m+}) in acidified solutions [15]. This is a special synthesis method where several different reactions between the reactants and intermediate products occur simultaneously leading to the formation of a final product with a complex structure. The reaction direction is often determined by slight differences in the structure and reactivity of the intermediates. The complementarity of the fragments that comprise the final product is the most important factor influencing the self-assembly reaction mechanism.

The acidity of $Z = \nu(H^+)/\nu(WO_4^{2-}) = 0.80$ and the stoichiometric amounts of reactants in an aqueous solution correspond to the formation of a heteropoly anion with the Peacock–Weakley type of structure $[X(W_5O_{18})_2]^{9-}$ [10-11]:

$$X^{3+} + 10\ WO_4^{2-} + 8\ H^+ \leftrightarrows [X(W_5O_{18})_2]^{9-} + 4\ H_2O,\ (X = Y, La–Lu).$$

To isolate the Y(III)-containing salt, a solution of Na_2WO_4 ($C_W = 0.1$ mol/L) was acidified to Z = 0.80, and then the solution of $Y(NO_3)_3$ was slowly added dropwise with vigorous stirring until the stoichiometric ratio of Y:W = 1:10 was reached. After that, 2-propanone was added in a volume equal to that of the homogeneous aqueous solution (50 v/v) resulting in the needle-like crystalline precipitate formation. The yield of the product was ~90%, with a loss of ~10%, likely due to the solubility of the salt during the precipitate washing with H_2O:2-propanone (1:1) solution. According to the results of chemical analysis and FTIR spectroscopy (Fig. 1, Table 1), the formula $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I) was assigned to the isolated precipitate.

The valence and deformation vibrations in the tungsten–oxygen framework in the FTIR spectrum of the air-dried sample of the salt (Fig. 1, Table 1) indicate the presence of a heteropoly anion with a Peacock–Weakley type of structure [2, 10-11].

According to single crystal X-ray analysis data [2], in the anion $[Y(W_5O_{18})_2]^{9-}$, two lacunary tetradentate pentatungstate anions $W_5O_{18}^{6-}$ are coordinated to the

Y(III)-heteroatom, forming a coordination polyhedron in the shape of a square antiprism. Thus, the coordination polyhedron of Y^{3+} consists of 8 oxygen atoms bound to the tungsten atoms of the two lacunary pentatungstate anions, distinguishing this type of heteropoly anion from others. In other heteropoly compounds, the coordination number of the heteroatom Y^{3+} is also 8, achieved through the coordination of oxygen atoms from lacunary isopoly anions and the coordination of H_2O molecules to Y^{3+} ion. For example, the anion $[Y_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{8-}$ consists of a fragment {W22} (two lacunary derivatives of the heteropoly anion with the Keggin-type structure, bound by two shared oxygen atoms) and two Y^{3+} ions, each coordinated by three oxygen atoms from the anion and five H_2O molecules [3]. In the anion $[Y_8(CH_3COO)(H_2O)_{18}(As_2W_{19}O_{68})_4(W_2O_6)_2(WO_4)]^{43-}$, H_2O ligands also complete the coordination spheres of the Y^{3+} cations [16].

Currently, microscopic studies are an effective mechanism for determining the single-phase nature of synthesized salts when it is impossible to do so using X-ray diffraction. Microscopic analysis showed that the surface of the salt (I) grains has indistinct, blurred boundaries, and the grain size of the sample ranges from 200 to 450 nm (Fig. 2).

The uniform contrast of the salt (I) surface during scanning in the backscattered electron (BEC) mode indicates the phase purity of the obtained salt (Fig. 3).

On the microphotographs of the powder of salt (I) under characteristic X-ray emission, there are no areas with different surface morphology and a uniform distribution of Y, Na, W, and O is observed without segregation or liquefaction (the present inhomogeneities are explained by the different surface topography of the

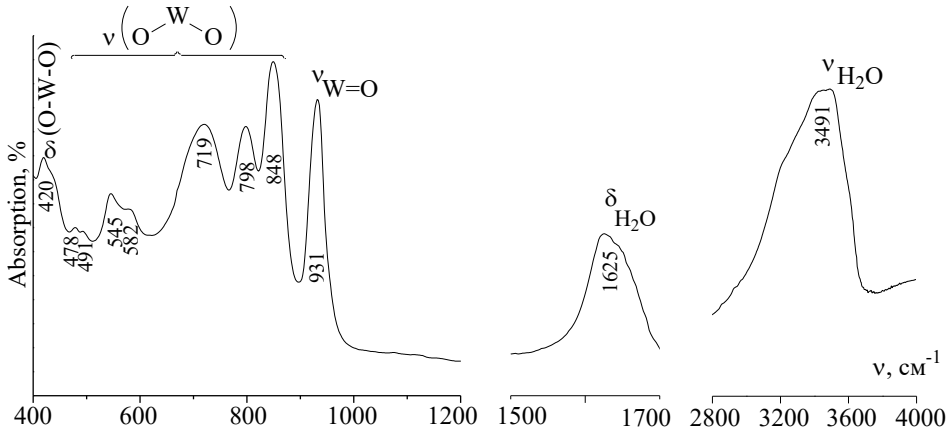

Fig. 1. FTIR spectrum of $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I) (in KBr).

Table 1.

Wavenumbers of absorption maxima (cm^{-1}) in the FTIR spectra of salts with the $[X(W_5O_{18})_2]^{9-}$ anion (in KBr).

X*	δ(O–W–O)	ν(O–W–O)						ν(W=O)
Y	420	491	545	582	719	798	848	931
Y'	422	490	547	615	707	782	845	940
Gd	417	488	543	585	708	783	844	944
Er	421	492	548	587	715	784	848	935
Tm	422	492	544	582	715	791	849	933
Yb	421	490	547	585	710	792	848	934

**Note:* Y – synthesized salt $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I); Y', Gd, Er, Tm, Yb – $Na_9[X(W_5O_{18})_2]\cdot 35H_2O$ (X = Y [2], Gd [10], Er [10], Tm [11], Yb [11]).

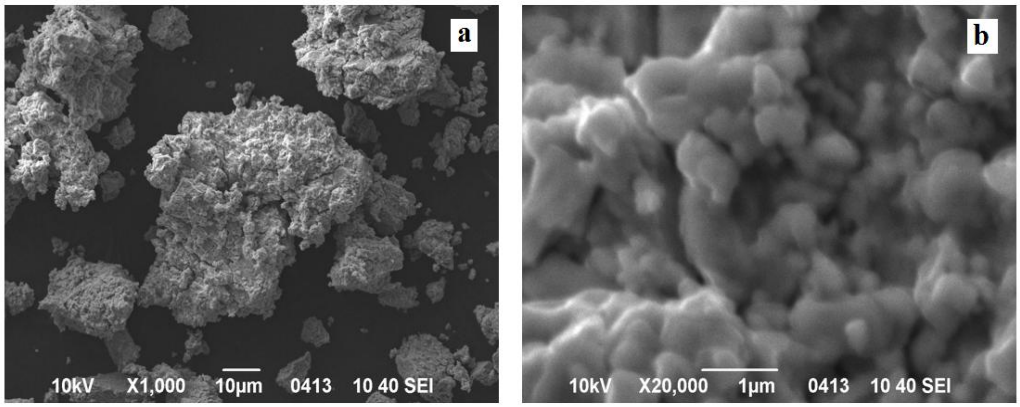

Fig. 2. SEM image of the surface of $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I) powder:(a) ×1,000; (b) ×20,000.

sample) (Fig. 4). This result also indicates the successful synthesis of a single-phase sample of the salt.

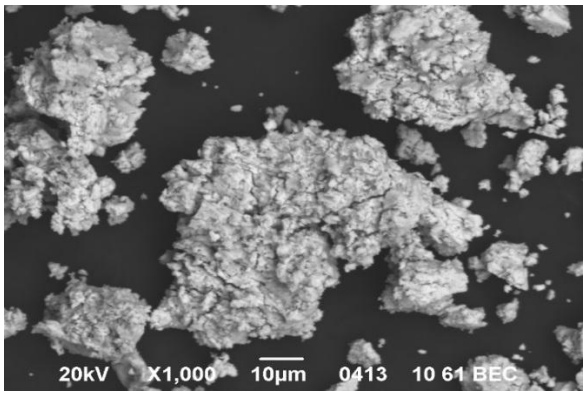

Fig. 3. Surface image of the powder (I) in BEC mode (×1,000).

Micrographs of salt (I) powder in characteristic X-rays show no areas with different surface morphology and a uniform distribution of Y, Na, W, and O without segregation and liquation (the existing inhomogeneities are explained by the various surface topography of the sample) (Fig. 4). This result also indicates that a single-phase salt sample was obtained.

The synthesis procedure for heteropoly decatungstolanthanidate(III) salts, most used for obtaining crystalline salts, was proposed by R.D. Peacock and T.J.R. Weakley in 1971 [1]. According to their procedure, a Na_2WO_4 solution is acidified with acetic acid to a pH of 7.0–7.2, and lanthanide nitrates or chlorides are added at $T = 90^0C$ with vigorous stirring. The crystalline precipitate forms either through slow crystallization at room temperature or after cooling the solution to 5^0C. The resulting crystalline precipitate is typically an acidic salt $Na_7H_2[X(W_5O_{18})_2]\cdot nH_2O$. However, as demonstrated in [17], the use of this procedure leads to the formation of a mixture of products instead of a single-phase sample. The salt with the Peacock–Weakley type of anion is the major product of the synthesis, but crystallization of sodium paratungstate B and a mixed-ligand heteropoly compound $Na_{12}H[(W_5O_{18})Tb(H_2W_{11}O_{39})]\cdot 42H_2O$ also occurs. To avoid the possibility of obtaining a multiphase product, a synthesis procedure developed for isolating heteropoly tungstolanthanidates(III) with the $[Ln(W_5O_{18})_2]^{9-}$ (Ln is a lanthanide) anion was elaborated [10-11], where the formation of a single-phase product is achieved through precipitation by 2-propanone adding. The proposed procedure made it possible to isolate an individual salt with a Y(III) heteroatom, $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I).

To obtain heteropoly salts with NH_4^+, K^+, Mg^{2+}, or Zn^{2+} cations and the anion $[Y(W_5O_{18})_2]^{9-}$, a slight excess (in the case of NH_4^+ and K^+) or stoichiometric amount (in the case of Mg^{2+} and Zn^{2+}) of solutions of NH_4NO_3, KNO_3, $Mg(NO_3)_2$, and $ZnSO_4$ was added to a freshly prepared solution of $Na_9[Y(W_5O_{18})_2]$ (V = 100 mL, C = 0.01 mol/L).

It has been established that the NH_4NO_3 solution addition does not lead to the formation of heteropoly tungstate with the NH_4^+ cation and an anion with the Peacock–Weakley type of structure. According to single-crystal X-ray diffraction analysis, the crystallization of the double sodium-ammonium paratungstate B $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (II) occurs. In the case of adding K^+, Mg^{2+}, or Zn^{2+} cations to the solutions of $[Y(W_5O_{18})_2]^{9-}$, salts with the paratungstate B anion are also formed – $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (III), $Mg_5[W_{12}O_{40}(OH)_2]\cdot 41H_2O$ (IV), and $Zn_5[W_{12}O_{40}(OH)_2]\cdot 35H_2O$ (V), the compositions of which have been established through chemical analysis and FTIR spectroscopy. This supports the hypothesis that in the A^+–Y^{3+}–WO_4^{2-} –H^+–H_2O ($A^+ = NH_4^+$, K^+) and M^{2+}–Y^{3+}–WO_4^{2-}–H^+–H_2O ($M^{2+} = Mg^{2+}$, Zn^{2+}) systems, the heteropoly anion $[Y(W_5O_{18})_2]^{9-}$ is formed through the generation of the paratungstate B anion as an intermediate species during the acidification of the orthotungstate anion solution. The solubility of the paratungstate B salts of NH_4^+, K^+, Mg^{2+}, or Zn^{2+} is lower compared to the sodium salt, leading to the formation of crystalline salts with the $[W_{12}O_{40}(OH)_2]^{10-}$ anion:

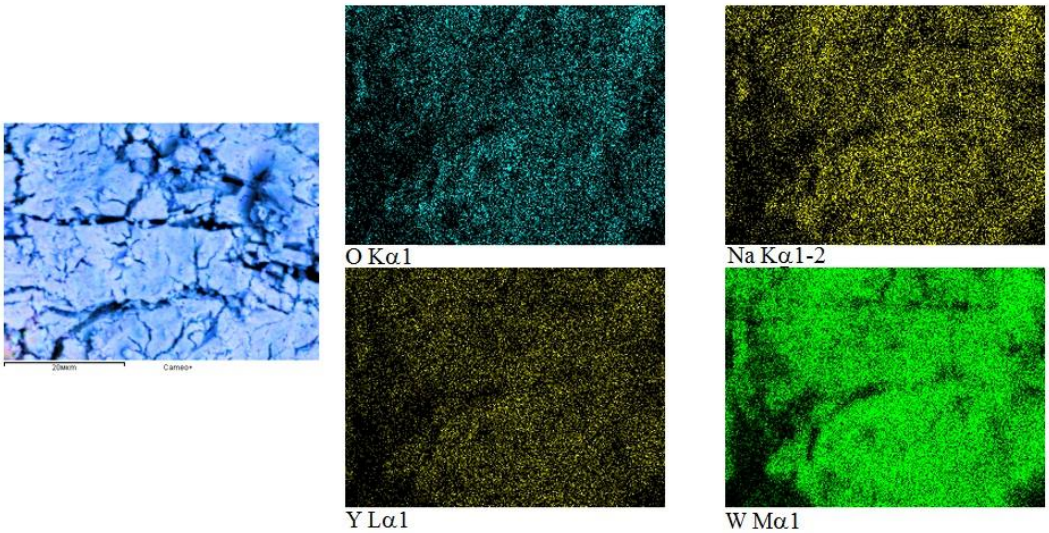

Fig. 4. SEM image of the surface of $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (I) powder in characteristic X-ray emission (Y Lα1, Na Kα1-2, W Mα1, and O Kα1).

$$10\ K^+ + 12/10\ [Y(W_5O_{18})_2]^{9-} + 3.2\ H_2O = K_{10}[W_{12}O_{40}(OH)_2] + 12/10\ Y^{3+} + 4.4\ OH^-;$$

$$2\ Na^+ + 8\ NH_4^+ + 12/10\ [Y(W_5O_{18})_2]^- + 3.2\ H_2O = Na_2(NH_4)_8[W_{12}O_{40}(OH)_2] + 12/10\ Y^{3+} + 4.4\ OH^-;$$

$$5\ M^{2+} + 12/10\ [Y(W_5O_{18})_2]^{9-} + 3.2\ H_2O = M_5[W_{12}O_{40}(OH)_2] + 12/10\ Y^{3+} + 4.4\ OH^-,$$

$$M^{2+} = Mg^{2+}, Zn^{2+}.$$

The simultaneous presence of isopoly tungstate and heteropoly tungstate anions in solutions with the same acidity has been observed previously. For example, during the study of interactions in the systems Ni^{2+}–WO_4^{2-}–H^+(Z=1.00)–H_2O [18, 19] and Ni^{2+}–MoO_4^{2-}–H^+(Z=1.00)–H_2O [20, 21], single-phase heteropoly tungstate compounds $Na_4[Ni(OH)_6M_6O_{18}]\cdot 16H_2O$ (M = W or Mo) with an Anderson-type anion [18, 20] were obtained using Na_2WO_4. However, the use of K_2WO_4 solution led to the simultaneous crystallization of a mixture of double potassium–nickel(II) salts with the paratungstate B anion, $K_6Ni_2[W_{12}O_{40}(OH)_2]\cdot 22H_2O$, and the heteropoly hexatungstonickelate(II) anion, $K_3Ni_{0.5}[Ni(OH)_6W_6O_{18}]\cdot 12H_2O$ [19]. Additionally, hydrolytic transformations of one isopoly anion into another can occur in solutions. For instance, in [22], the conditions for the hydrolytic conversion of decatungstate anion to paratungstate B anion were established, as confirmed by the isolation of salts $(H_3O)_3[\{K(H_2O)\}_2\{Na_2(H_2O)_8\}_2(Na_{0.5}H_2O)_2W_{12}O_{40}(OH)_2]\cdot 6H_2O$ and $(H_3O)_2[\{K(H_2O)_4\}_2\{Na_3(H_2O)_9\}_2W_{12}O_{40}(OH)_2]\cdot 2H_2O$ from freshly prepared $Na_4[W_{10}O_{32}]$ in a CH_3OONa/CH_3COOH buffer solution (pH 5.5):

$$12/10\ [W_{10}O_{32}]^{4-} + 3.6\ H_2O = H_x[W_{12}O_{40}(OH)_2]^{(10-x)-} + (5.2–x)\ H^+\ (x = 2, 3).$$

In our case, the addition of NH_4^+, K^+, Mg^{2+}, and Zn^{2+} cations caused a shift in equilibrium, leading to the formation of salts with the paratungstate B anion:

$$12/10\ [Y(W_5O_{18})_2]^{9-} + 3{,}2\ H_2O = [W_{12}O_{40}(OH)_2]^{10-} + 12/10\ Y^{3+} + 4.4\ OH^-.$$

This shift in equilibrium is likely a result of the binding of the added cations with the $[W_{12}O_{40}(OH)_2]^{10-}$ anion, leading to the formation of salts with lower solubility compared to the salts containing the heteropoly anion $[Y(W_5O_{18})_2]^{9-}$.

The obtained result is consistent with the data from [23], in which a double salt with the $[W_{12}O_{40}(OH)_2]^{10-}$ anion, $[Cu(en)_2Na_8(H_2O)_{28}(W_{12}O_{40}(OH)_2)]\cdot 4H_2O$ (en – ethylenediamine), was synthesized from a solution of $[Cu(en)]SO_4$ and a heteropoly salt containing the anion with the Peacock–Weakley type of structure, $Na_9[Eu(W_5O_{18})_2]\cdot nH_2O$.

The identification of anions in the synthesized crystalline salts was carried out by comparing the FTIR spectra (Fig. 5) with those reported in the literature [24, 25] for compounds whose structures were reliably established by X-ray crystallography. The similarity of the FTIR spectra of salts II, III, IV, V, and sodium

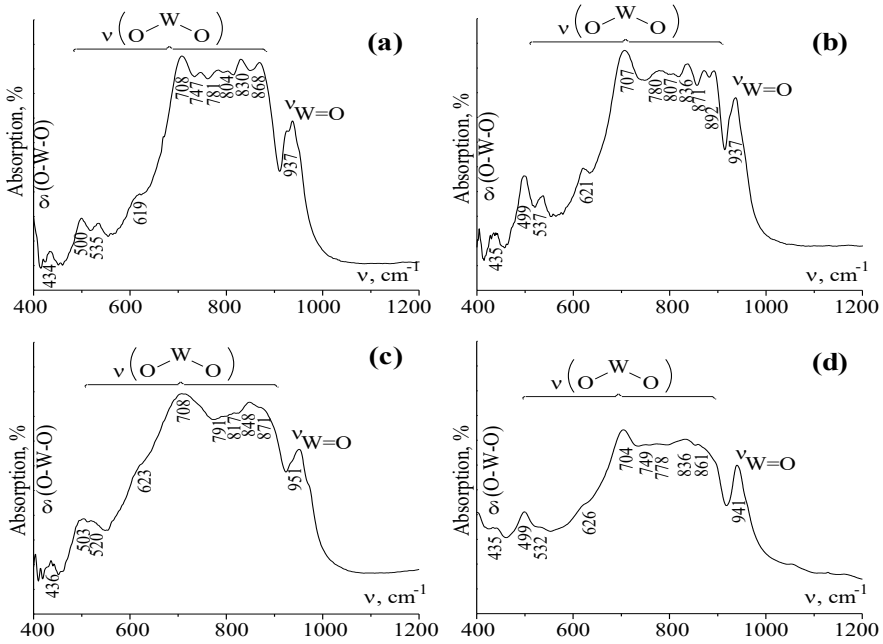

Fig. 5. FTIR spectra of the salts isolated from the A^{n+}–Y^{3+}–WO_4^{2-}–H^+–H_2O ($A^{n+} = NH_4^+$, K^+, Mg^{2+}, Zn^{2+}) system: (a) II, (b) III, (c) IV, and (d) V (in KBr).

paratungstate B $Na_{10}[W_{12}O_{40}(OH)_2]\cdot 26H_2O$ [24] and nickel(II) paratungstate B $Ni_5[W_{12}O_{40}(OH)_2]\cdot 37H_2O$ [25] in the range of tungsten-oxygen framework vibrations (400–1000 cm^{-1}) confirms the presence of the $[W_{12}O_{40}(OH)_2]^{10-}$ anion in the synthesized samples.

The crystals of II and III were used for single-crystal X-ray diffraction analysis. The main crystallographic data obtained are shown in Table 2.

X-ray crystallographic analysis of single crystals of salt II revealed that all metal atoms in the structure are in an octahedral environment. Fig. 6a shows the numbering scheme and thermal ellipsoids in the structure of II. The crystallographic data for II correspond to the structure described in [26] and are like those of the double sodium-ammonium paratungstate B [27]. The crystal packing of II is shown in Fig. 6b.

Table 2.

Crystallographic data and results of the crystal structure refinement for single crystals of compounds II and III.

Empirical formula	$H_{58}N_8Na_2O_{54}W_{12}$ (II)	$H_{28}K_{10}O_{54}W_{12}$ (III)
Formula weight M_r, a.m.u.	3286.72	3489.42
Temperature, K	200(2)	293(2)
Wavelength MoKα, Å	0.71073	
Crystal system, space group	Orthorhombic, P bca	Monoclinic, P $2_1/c$
Unit cell dimensions (Å)	a = 14.0631(6), b = 15.6713(5), c = 22.9147(16)	a = 11.5049(6), b = 14.3008(7), c = 15.4567(10)
α, β, γ (°)	90, 90, 90	90, 105.889(7), 90
Cell volume V, $Å^3$	5050.1(4)	2445.9(2)
Z, d_{calc} (g/cm^3)	4, 4.323	2, 4.738
Absorption coefficient μ(MoKα), mm^{-1}	27.356	29.066
F(000)	5824	3076
Crystal size, mm	0.16×0.08×0.02	0.15×0.12×0.08
θ range for data collection	3.15° ≤ □ ≤ 30.00°	3.09° ≤ θ ≤ 29.99°
Index ranges	–19≤*h*≤19, –22≤*k*≤21, –32≤*l*≤32	–16≤h≤11, –15≤k≤20, –21≤l≤21
Reflections collected / unique	30781 / 6955 (R_{int} = 0.1769)	16175 / 6869 (R_{int} = 0.1880)
Completeness to θ = 30.00°	94.4%	96.2%
Transmission T_{max}/T_{min}	0.6107 / 0.0969	0.2045 / 0.0974
Refinement method	Full-matrix least-squares on F^2	
Data / parameters	6955 / 188	6869 / 343
Goodness-of-fit S on F^2	0.977	0.992
Final R indices ($I>2\sigma_I$)	R_1 = 0.1017, wR^2 = 0.2324	R_1 = 0.0672, wR^2 = 0.1401
R indices (all data)	R_1 = 0.1300, wR^2 = 0.2549	R_1 = 0.1371, wR^2 = 0.1844
Largest diff. peak / hole $\Delta\rho_{max}/\Delta\rho_{min}$, $e/Å^3$	4.192 / –4.220	4.457 / –3.474

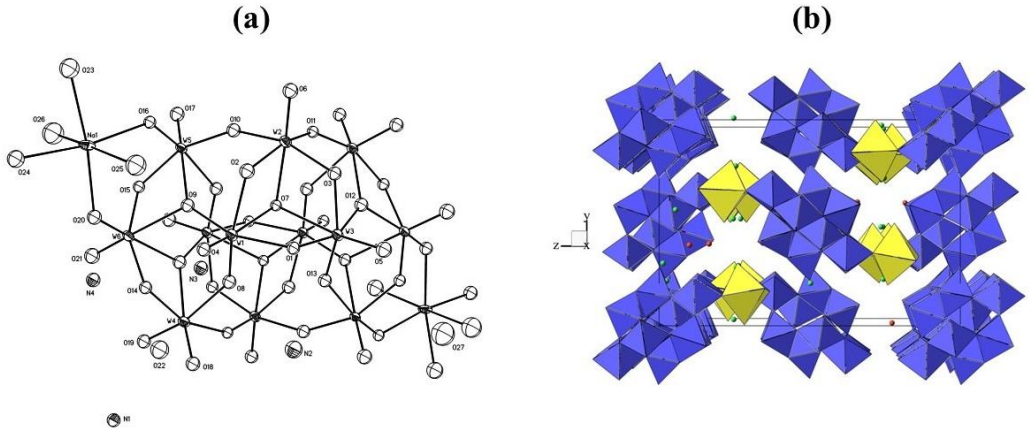

Fig. 6. Crystal structure of II: (a) Atom numbering scheme and thermal ellipsoids (40% probability level, symmetrically equivalent atoms are omitted for clarity); (b) Polyhedral representation of II along the *x*-axis, color coding: {WO_6}, blue octahedra; {NaO_6}, yellow octahedra; O (from non-coordinated H_2O molecules), red balls; N (NH_4^+), turquoise balls.

The comparison of the crystallographic data for salt II and the compounds previously in [26-27] is presented in Table 3. Despite the different types of space groups, the bond lengths and valence angles between oxygen and tungsten atoms in the $[W_{12}O_{40}(OH)_2]^{10-}$ anion are quite similar.

In Fig. 7, the structure of the basic structural unit for III is shown. The paratungstate B anion in the structure has a centrosymmetric arrangement, just like in $K_{10}[W_{12}O_{40}(OH)_2]\cdot 7.5H_2O$ [28] and $K_{10}[W_{12}O_{40}(OH)_2]\cdot 10H_2O$ [29]. The compounds themselves differ in the quantitative content of crystallization water molecules.

Structural data for III (Table 2) and $K_{10}[W_{12}O_{40}(OH)_2]\cdot 7.5H_2O$ (M_r = 3406.3, T = 296 K, triclinic symmetry, P–1, a = 13.126, b = 16.274, c = 11.756 Å, α = 96.77, β = 90.04, γ = 77.77°, V = 2436.4 Å^3, Z = 2, d_x = 4.645 g·cm^{-3}) [28], $K_{10}[W_{12}O_{40}(OH)_2]\cdot 10H_2O$ (M_r = 3435.37, T = 293 K, triclinic symmetry, P–1, a = 11.62, b = 13.102, c = 16.32 Å, α = 77.7, β = 83.2, γ = 89.8°, V = 2410.49 Å^3, Z = 2, d_x = 4.739 g·cm^{-3}) [29] show differences in space group and crystal lattice parameters. The anion of paratungstate B in $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (III) has a centrosymmetric structure, just like in salts with different hydration compositions [28-29], but the distinction lies in the fact that all H_2O molecules are located in the coordination sphere of K^+ ions, and the structure of the salt is layered. The centrosymmetric anions are arranged in layers along the x = 0.5 planes with part of the KO_n polyhedra serving as "bridges" between the anions. The image of the layer is shown in Fig. 8a. Other KO_n polyhedra form a layer in the plane x = 0 (and in the equivalent x = 1 plane). The mutual arrangement of these layers is shown in Fig. 8b.

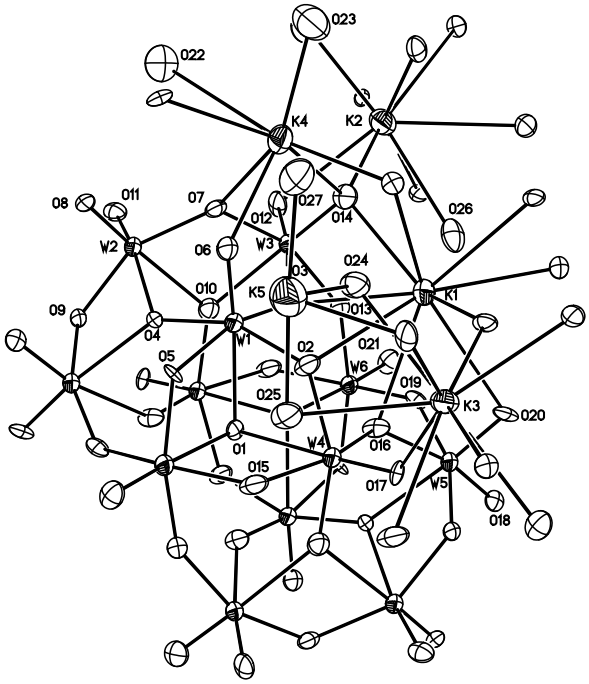

Fig. 7. Scheme of atom numbering and thermal vibration ellipsoids (probability level 30%) for III. Symmetrical equivalents of atoms are not numbered for clarity.

The salts II–V were studied using scanning electron microscopy. The surface micromorphology was investigated during scanning in the secondary electron mode, and the grain size of the samples after grinding did not exceed 1 Å (see Fig. S1). The single-phase nature of the synthesized salts with the paratungstate B anion was confirmed by the uniform contrast of the surface during the scanning of the samples in the backscattered electron mode (Fig. S2) and in the characteristic X-ray emission (Fig. S3).

Table 3.

Crystallographic data for salts $Na_2(NH_4)_8[H_2W_{12}O_{42}]\cdot 12H_2O$.

Parameter	II (this work)	[27]	[26]
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	P bca	$P2_1/c$	P bca
Unit cell dimensions, Å	a = 14.0631(6), b = 15.6713(5), c = 22.9147(16)	a = 12.0116(7), b = 14.0777(8), c = 15.5729(8)	a = 15.78, b = 22.93, c = 14.13
α, β, γ (°)	90, 90, 90	90, 105.6020, 90	90, 90, 90
V, Å^3	5050.1(4)	2536.3	5112.7(3)
Z	4	2	4
d_{calc}, g·cm^{-3}	4.323	4.304	4.27
d(W=O), Å	1.698–1.766	1.724–1.773	1.640–1.772
d(W–μ_3-O(H)), Å	2.244–2.260	2.251–2.253	2.209–2.292
d(W–μ_2-O), Å	1.773–2.195	1.813–2.191	1.779–2.244
d(W–μ_3-O), Å	1.913–2.292	1.892–2.240	1.920–2.265
d(Na–O), Å	2.350–2.458	2.319–2.478	2.330–2.431
∟(W–μ_3-O(H)–W), °	95.09–96.57	95.1–96.5	94.05–97.06
∟(W–μ_2-O–W), °	112.55–119.90 137.63–148.14	114.6–118.4 136.6–147.7	108.43–120.26 142.47–150.47
∟(W–μ_3-O–W), °	94.54–95.17 124.27–139.91	93.7–94.6 124.5–139.9	95.03–95.62 126.78–137.23

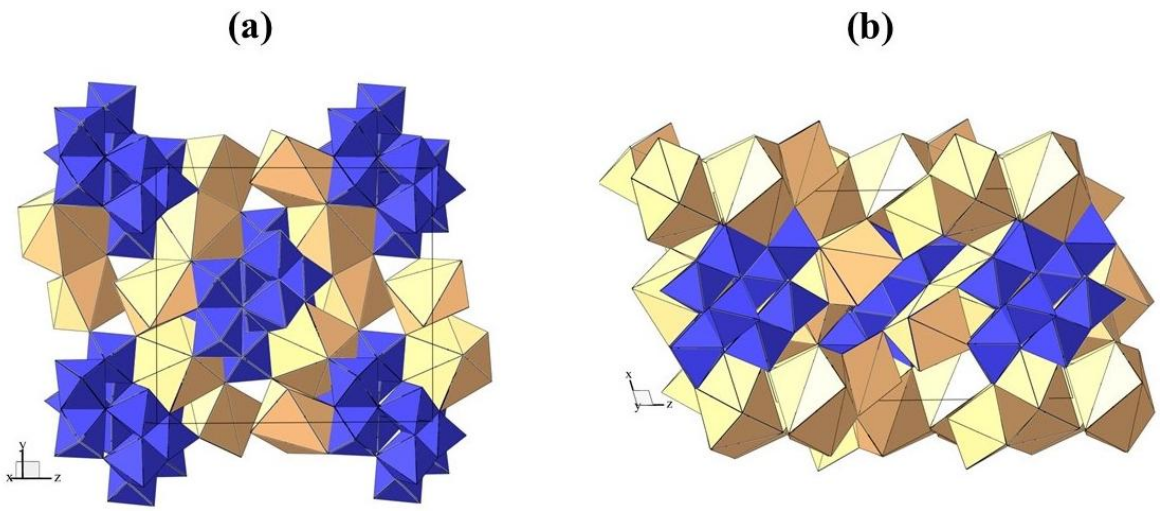

Fig. 8. Polyhedral representation of the structure of III: (a) polyhedral representation of a layer in III; (b) depiction of the packing of polyhedra in the structure of III along the *y*-axis. Color codes: {WO_6}, blue octahedra; {KO_n}, yellow polyhedra.

Conclusions

The studies made it possible to develop a new synthesis procedure for Y(III)-containing heteropoly tungstate (I) from an aqueous solution acidified to $Z = \nu(H^+)/\nu(WO_4^{2-}) = 0.80$, using precipitation with 2-propanone. The main advantage of the proposed procedure is the ability to obtain a normal salt. The presence of the heteropoly anion with the Peacock–Weakley type of structure in the synthesized salt $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ has been confirmed by FTIR spectroscopy. Scanning electron microscopy has confirmed the single-phase nature of the salt and shown that the grain size of $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ is in the range of 200–450 nm. The conditions for synthesizing salts II, III, IV, and V with cations NH_4^+, K^+, Mg^{2+}, Zn^{2+} and the paratungstate B anion from the solutions of the systems A^+–Y^{3+}–WO_4^{2-}–H^+–H_2O ($A^+ = NH_4^+$, K^+) and M^{2+}–Y^{3+}–WO_4^{2-}–H^+–H_2O ($M^{2+} = Mg^{2+}$, Zn^{2+}) have been established. The structure of the anion in the salts was determined by FTIR spectroscopy. The crystal structures of the single crystals of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (II) and $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (III) were studied by single-crystal X-ray diffraction analysis. The single-phase nature of the synthesized paratungstates B has been confirmed by uniform surface contrast during the scanning of the samples in the backscattered electron mode and characteristic X-ray emission.

Acknowledgments.

The research was carried out within the framework of the Fundamental Research Programme of the Ministry of Education and Science of Ukraine (Research Project No. 0122U000762). The authors express their gratitude to the Armed Forces of Ukraine, whose heroism makes it possible to continue research in Ukraine.

Supplementary materials.

The files containing crystallographic data for the structures of $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (CSD-433328) and $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (CSD-433329) have been deposited in The Cambridge Crystallographic Data Centre (CCDC). The file with electronic supplementary materials includes the results of the study of salts II–V using scanning electron microscopy.

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Фазоутворення у системах $A^+–Y^{3+}–WO_4^{2-}–H^+–H_2O$ ($A^+ = NH_4^+, K^+$) та $M^{2+}–Y^{3+}–WO_4^{2-}–H^+–H_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$). Синтез, ІЧ-спектроскопічний аналіз та визначення кристалічної будови солей із аніоном паравольфрамату Б, $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ та $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$

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Розроблено нову методику синтезу натрію гетерополідекавольфрамоітріату(III) $Na_9[Y(W_5O_{18})_2]\cdot 35H_2O$ (**I**) із водного розчину натрію вольфрамату, підкисленого до кислотності $Z = \nu(H^+)/\nu(WO_4^{2-}) = 0.80$ зі співвідношенням $\nu(Y):\nu(W) = 1:10$, та з додаванням 2-пропанону. Методом ІЧ-спектроскопії підтверджено наявність аніона зі структурою Пікока–Уіклі у складі виділеної солі. Мікроморфологію поверхні досліджено за допомогою скануючої електронної мікроскопії (СЕМ); було встановлено, що розмір зерен знаходиться в межах 200–450 нм. Однофазність синтезованої солі підтверджено однорідним контрастом поверхні у режимі зворотнорозсіяних електронів. Встановлено умови синтезу солей із аніоном паравольфрамату Б $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ (**II**), $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ (**III**) та $M_5[W_{12}O_{40}(OH)_2]\cdot nH_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$) (**IV, V**) із підкислених до $Z = 0.80$ водних розчинів систем $A^+–Y^{3+}–WO_4^{2-}–H^+–H_2O$ ($A = NH_4^+, K^+$) та $M^{2+}–Y^{3+}–WO_4^{2-}–H^+–H_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}$). Одержані солі охарактеризовано за допомогою елементного аналізу, СЕМ та ІЧ-спектроскопії. Кристалічну будову $Na_2(NH_4)_8[W_{12}O_{40}(OH)_2]\cdot 12H_2O$ **(II)** ($M_r = 3286.72$, орторомбічна сингонія, Pbca, $a = 14.0631(6)$ Å, $b = 15.6713(5)$ Å, $c = 22.9147(16)$ Å, $V = 5050.1(4)$ Å^3 за $T = 200(2)$ K, $Z = 4$, $d_{розр.} = 4.323$ г/см^3) та $K_{10}[W_{12}O_{40}(OH)_2]\cdot 13H_2O$ **(III)** ($M_r = 3489.42$, моноклінна сингонія, $P2_1/c$, $a = 11.5049(6)$ Å, $b = 14.3008(7)$ Å, $c = 15.4567(10)$ Å, $\beta = 105.889(7)°$, $V = 2445.9(2)$ Å^3 за $T = 293(2)$ K, $Z = 2$, $d_{розр.} = 4.738$ г/см^3) встановлено методом рентгеноструктурного аналізу з монокристалів.

Ключові слова: поліоксометалати, гетерополівольфрамат, ітрій, структура Пікока–Уіклі, аніон паравольфрамату Б, скануюча електронна мікроскопія, рентгеноструктурний аналіз монокристалів, синтез.